Controlled Release Profile of Imidacloprid-β-Cyclodextrin Inclusion Complex Embedded Polypropylene Filament Yarns

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ABSTRACT

Imidacloprid-β-cyclodextrin (IMI-β-CD) inclusion complex was synthesized and effectively incorporated into filament yarns of polypropylene. The physical and thermal properties of IMI-β-CD inclusion complex were determined by Fourier transform infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. According to the results, formation of the inclusion complex was achieved along with enhanced thermal stability. The release profile of imidacloprid was monitored by high-performance chromatography measurements. Dissolution time of the IMI-β-CD inclusion complex was increased to 5 times that of the neat imidacloprid (from 9 h to 48 h). Poylpropylene filament yarns containing 3 wt.% IMI-β-CD inclusion complex released 84 wt.% of IMI within 21 days.

INTRODUCTION

The steady increase in world population and environmental pollution and the gradual decrease of natural resources have led to the concept of "sustainable efficient agriculture" and humankind has made progress toward this goal. Development of agrotextile materials is one such effort. Production of innovative agrotextile materials enabling reduced use of pesticides would be a very important step in the field of sustainable efficient agriculture.

There are many studies concerning pesticide containing textiles in the literature. In general pesticides have been used only in protective clothes for insect repellency. Cotton fabrics with repellent activity have been achieved by conventional methods such as padding and coating [1-13] and by sol-gel techniques [14]. In order to achieve long-term efficiency, insect repellents are applied in encapsulated form, e.g., either as microcapsules [2,4] or β-cyclodextrin (β-CD) inclusion complexes [3,10-13].

An inclusion complex is a type of supramolecular complex, in which one part of a molecule, "the guest" is enclosed within another molecular structure, "the host". β-cyclodextrins, which are cyclic oligosaccharides obtained from starch by enzymatic cyclization, have the ability to form inclusion complexes with suitable guest molecules because of their hydrophobic cavities [15]. In recent years, β-CDs have been extensively used in textile applications [16,17].

Imidacloprid (IMI) is a chloronicotinyl insecticide that is commonly applied as a systemic pesticide for controlling many species of sucking insects, termites and other chewing pests [18-20]. Owing to its physical properties and high insecticidal activity at low application rates, imidacloprid has drawn attention as an efficient pesticide. Because imidacloprid is routinely sprayed over fields to protect crops, it is directly released into the environment. In order to enhance imidacloprid efficacy, reduce quantities required, eliminate the need for repeated applications, and thus reduce environmental pollution, development of imidacloprid formulations possessing controlled release properties would be desirable.

While there are studies in the literature involving the chemical and physical characterization of IMI-β-CD inclusion complexes, [21,22], there are none related to their use in textiles for agricultural applications. This paper presents for the first time controlled release IMI-β-CD embedded within polypropylene (PP) filaments. IMI-β-CD inclusion complex was synthesized and incorporated into PP through melt-spinning. Afterwards, controlled release properties of the neat imidacloprid, IMI-β-CD inclusion complex, and PP filaments containing the inclusion complex were investigated.

MATERIALS AND METHODS

Materials

Imidacloprid ((1-[(6-chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine), $C_9H_{10}ClN_5O_2$, molecular weight: 255.66 g/mol, Confidor® SC 350 containing 350 g/l imidacloprid, Bayer Cropscience, Germany) (*Figure 1(a)*), technical grade β-cyclodextrin ($C_{42}H_{70}O_{35}$, molecular weight: 1134.98 g/mol, Nearfesh TS Pwd, Nearchimica spa Italy) (*Figure 1(b)*), homopolymer polypropylene (Moplen HP500N, $MFI_{230^{\circ}C/2.16\ kg}$: 12 g/10 min, T_m: 161°C, LyondellBasell Industries, Italy) were used in the study. Dichloromethane (HPLC grade, Carlo Erba, Italy) was used for extraction. All other chemicals used were of analytical grade.

Methods

Preparation of Imidacloprid-β-Cyclodextrin Inclusion Complex

Imidacloprid (6.8 g) was suspended in 100 ml distilled water by stirring at ambient temperature. β-cyclodextrin (21.1 g) was added to the aqueous suspension and the mixture was stirred for 0.5 h at 60°C. Subsequently, vacuum distillation was employed. Possible structure of imidacloprid-β-cyclodextrin inclusion complex is shown in *Figure 1(c).*

Preparation of Physical Mixture of Imidacloprid and β-Cyclodextrin

In order to determine the formation mechanism of the inclusion complex, imidacloprid and β-cyclodextrin were physically blended together at room temperature and used for FT-IR analysis.

Preparation of Polypropylene and Imidacloprid-β-Cyclodextrin Inclusion Complex

In order to obtain a homogeneous mixture, a blend of PP/IMI-β-CD inclusion complex (97/3 w/w) was generated using a co-rotating intermeshing twin screw extruder (Thermo Scientific™ Process 11, Germany, Ø: 11 mm, L/D ratio: 40). The temperature of the extruder barrel zones was set to 7 x 180°C, the blend was fed at a screw speed of 5 rpm and extruded at screw speed of 175 rpm.

Based on the application amount of imidacloprid in agricultural fields, 3 wt.% IMI-β-CD inclusion complex was incorporated into the PP filaments [23,24]. Filament yarn production was carried out by spinning the previously generated polymer blend on a Collin E20 T-MP-IS single screw extruder (Dr. Collin GmbH, Germany, Ø: 20 mm, L/D ratio: 25) and a Collin CMF 100 melt-spinning system (*Figure 2, Table I).* The barrel temperature profile was as follows: 200°C, 205°C, 210°C, 220°C, 3 x 230°C. The samples were extruded using a circular spinneret with 24 holes. Cooling of the extruded filaments was achieved with cross-flow air quenching at a temperature of 12ºC. The as-spun filaments were four stage drawn to an overall draw ratio of 2.5, in a continuous spin-drawing process. Take-up speeds were varied from 316 to 799 m/min with the throughput adjusted to yield a linear density of 34 tex.

The PP/(IMI-β-CD) (97/3 w/w) filament yarns were left for 48 h under standard atmospheric conditions before the tests (relative humidity: 65 ± 5%, temperature: 20 ± 2ºC.)

Characterization

FT-IR Analysis: The chemical structure of IMI, β-CD, and IMI-β-CD inclusion complex was investigated using a Perkin Elmer Spectrum 400 FT-IR spectrometer. Measurements were carried out using 32 scans in the 400 - 4000 cm^{-1} range with 4 cm^{-1} resolution.

Thermal Analyses: The thermal stability of IMI, β-CD and IMI-β-CD inclusion complex was determined by thermogravimetric analysis (TGA) using a Mettler Toledo thermal analyzer having a 951 TG module. Thermogravimetric analysis was carried out in the temperature range of 25 - 500°C in nitrogen atmosphere (flow rate = 60×10^{-6} m^3/min) at a heating rate of 20°C/min. A sample mass of 10 ± 2 mg was used.

Differential scanning calorimetry (DSC) studies were done using a Mettler Toledo STAR 822e instrument in the temperature range of 40-340°C in nitrogen atmosphere using a heating rate of 10°C/min. A sample mass of 5 ± 2 mg was used.

High-performance Liquid Chromatography (HPLC) Analysis: HPLC measurements were performed on a Agilent Technology HPLC 1260 Series instrument at room temperature. ChemStation software was used for data acquisition and processing. The maximum wavelength of the UV-VIS detector was 270 nm for imidacloprid. Isocratic elution was carried out in a C18 universal column with acetonitrile/water (50:50 v/v) mobile phase at a flow rate of 0.5 ml/min.

Dissolution profiles of the IMI and IMI-β-CD inclusion complex were determined as follows: 15 mg of samples were soaked into 200 ml of distilled water and at different time intervals (0, 1, 3, 6, 9, 12, 24, 48 and 96 h) aliquots of 0.5 ml were removed.The injector volume for the sample was 20 µL. The unused sample portions were returned to the flasks [25].

Dichloromethane was used as the extraction solvent for rapid determination of imidacloprid presence within the polypropylene matrix. After addition of anhydrous sodium sulfate (about 15 g) and dichloromethane (50 mL) in PP/IMI-β-CD yarn (7 g) and ultrasonification of the mixture (60 min), the dichloromethane extract was evaporated to dryness under reduced pressure in a rotary evaporator at 40°C [26].

In order to determine the time dependent release of imidacloprid from yarn under real conditions, 35 g of PP/IMI-β-CD (97/3 w/w) filament yarns were added to 250 ml distilled water in a stoppered conical flask and held without shaking the flask throughout the release experiment. At time intervals of 0, 1, 3, 5, 7, 14 and 21 days, aliquots of 0.5 ml were removed. Before removing the aliquots, the conical flasks were shaken gently to insure adequate mixing of the contents. The injector sample volume was 20 µL. The unused sample portions were returned to the flasks.

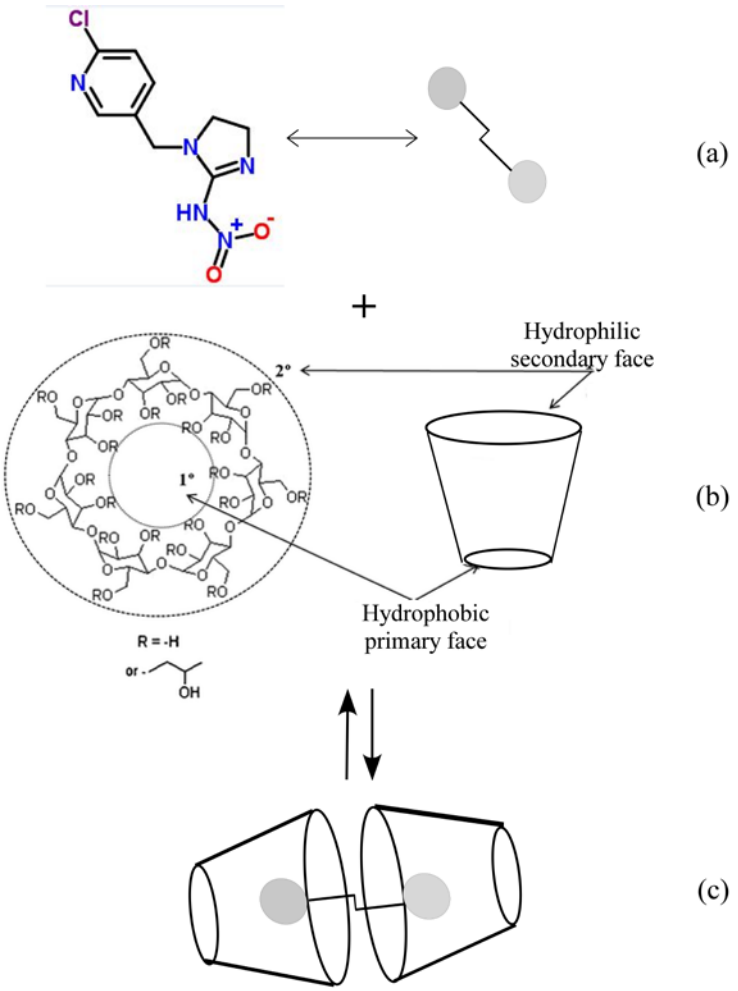

FIGURE 1. The structure of (a) imidacloprid (IMI), (b) β-cyclodextrin (β-CD) and (c) imidacloprid-β-cyclodextrin (IMI-β-CD) inclusion complex.

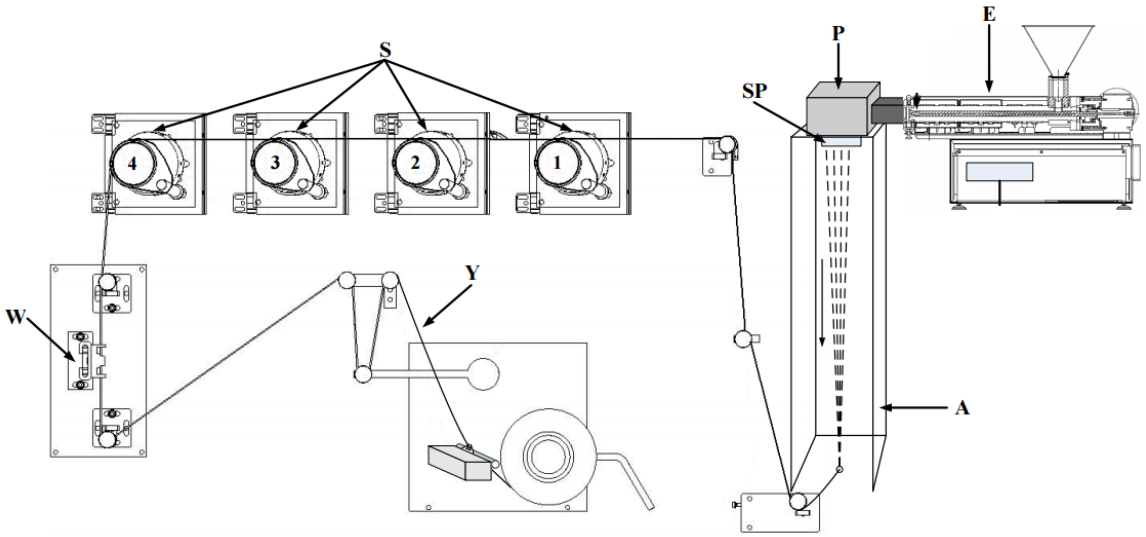

FIGURE 2. Collin CMF 100 melt-spinning system. E: extruder, P: melting pump, SP: spinneret, A: air quench cabinet, S: stretching godets (godet No 1, No 2, No 3, No 4), W: whirling unit, Y: yarn.

TABLE I. Constant processing parameters used in melt-spinning.

Parameter	Extrusion				Spinning				
	Hole diameter, mm	Hole length, mm	Extruder pressure, MPa	Screw speed, rpm	Stretching godets temperature, °C/speed, rpm				Drawing ratio
					No.1	No.2	No.3	No.4	
Value	0.45	1.3	3	60	81/316	97/632	107/727	120/799	2.5

RESULTS AND DISCUSSION

Chemical Structure of Imidacloprid and Imidacloprid-β-Cyclodextrin Inclusion Complex

The structure of IMI is similar to a dumbbell structure. Therefore, it is possible that two β-CD units interact with one IMI unit to form a 2:1 inclusion complex, as shown in *Figure 1(c).*

The FT-IR spectrograms of IMI, β-CD, their physical mixture and IMI-β-CD inclusion complex are presented in *Figure 3.* The pure IMI showed characteristic vibration peaks at 1562 cm^{-1} and 3350 cm^{-1}, which are related to -NO_2 and -NH stretches (*Figure 3(a)*). The characteristic band observed at 1031 cm^{-1} is assigned to stretching vibration of C−O−C bonds, which is associated with β-CD (*Figure 3(b)*). In addition, β-CD demonstrated bands at 2922 cm^{-1} and 3414 cm^{-1}, which are assigned to -CH_2 and -OH stretching vibrations, respectively [25,27]. All of the above characteristic peaks can be found in physical mixtures of IMI and β-CD (*Figure 3(c)*). The FT-IR spectrum for the IMI-β-CD inclusion complex is similar to that of the pure β-CD (*Figure 3(d)*), indicating formation of the inclusion complex. This is a common phenomenon observed by many researchers when synthesizing the inclusion complex between β-CD (host) and guest molecules [28-31].

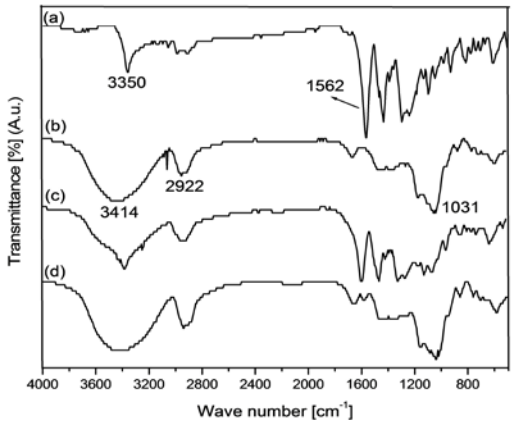

FIGURE 3. FT-IR spectrograms of (a) IMI, (b) β-CD, (c) physical mixture of IMI and β-CD, (d) IMI-β-CD inclusion complex.

Thermal Behavior of Imidacloprid and Imidacloprid-β-Cyclodextrin Inclusion Complex

Thermal stability of the pesticide is one of the most critical steps in production of functional fibers with controlled release properties. Pesticides must be stable not only during storage and application but also during the manufacturing process. Any degradation reactions will reduce the effectiveness of the pesticide.

The TGA graphs of the chemicals (IMI and β-CD) and the synthesized IMI-β-CD inclusion complex are depicted in *Figure 4*. IMI starts to decompose at ca. 261°C. β-CD exhibits two separate weight losses due to loss of water molecules located in the cavity of β-CD at 100°C followed by the decomposition of macrocycles at 335°C [32]. The IMI-β-CD inclusion complex also loses water at 100°C. The second decomposition for the IMI-β-CD inclusion complex is around 309°C. This phenomenon suggests that formation of inclusion complex increases the thermal stability of imidacloprid.

Figure 5 shows that the DSC thermogram of β-CD has broad endothermic peaks just above 100 °C and just above 300°C corresponding to the release of water from β-CD and decomposition of β-CD, respectively [33]. The DSC thermogram of IMI exhibits a sharp endothermic peak at approximately 133°C, corresponding to the melting of IMI. The large exotherm centered at 260°C is the decomposition temperature of IMI. The melting temperature of IMI hardly appeared in the IMI-β-CD inclusion complex. This observation confirms the formation of the inclusion complex of IMI with β-CD since a shift or disappearance of the melting peak of the pure guest molecule is taken as conclusive evidence of inclusion complex formation [34].

Based on the thermal analyses results, IMI-β-CD inclusion complex can be melt processed in PP without encountering thermal degradation since PP is extruded at a temperature range of 190 - 220°C.

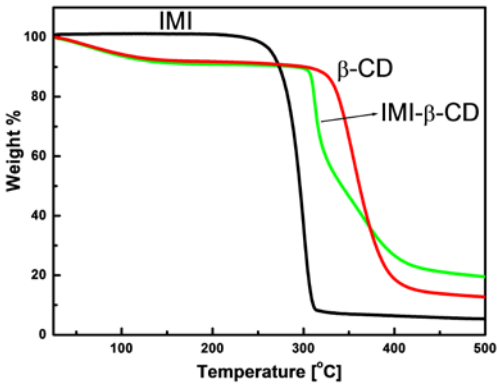

FIGURE 4. TGA graphs of IMI, β-CD and IMI-β-CD inclusion complex.

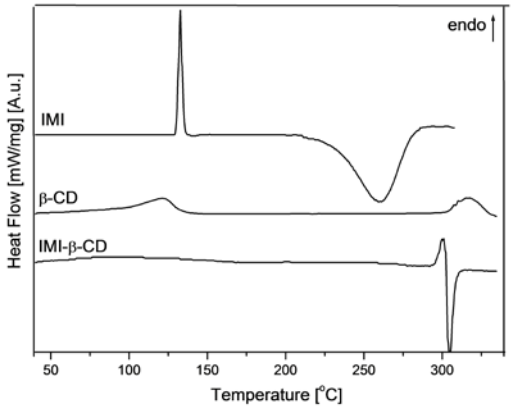

FIGURE 5. DSC thermograms of IMI, β-CD and IMI-β-CD inclusion complex.

Controlled Release of Imidacloprid and Imidacloprid-β-Cyclodextrin Inclusion Complex

A standard solution with 3.5 ppm imidacloprid was prepared and used for HPLC instrument calibration and sample calculation. Retention time of imidacloprid was found to be 7.1 min.

Before determination of chemical release profile of PP/IMI-β-CD filament yarns, the dissolution profile of IMI and IMI-β-CD inclusion complex in distilled water was studied. As shown in *Figure 6*, IMI dissolution is completed within 9 h. The inclusion complex of IMI with β-CD increases the dissolution time up to 48 h (an increase of greater than 5 times).

Use of β-CD as an inclusion compound offers the following advantages [21,35,36]: β-CD complexes could mask undesirable effects of the guest molecule. When a guest is included in a β-CD molecule, it is isolated and prevented from coming into direct contact where it could cause undesired side-effects such as irritation. Chemical toxic effects could also be reduced or eliminated. β-CD usage also enables conversion of liquid chemicals into solid ones, which makes easier melt processing possible. In addition, β-CD inclusion complexes improve the thermal stability of chemicals, significant in terms of melt processing. More important is the fact that β-CD inclusion complexes provide controlled and prolonged release of chemicals. Because of these advantages, the IMI-β-CD inclusion complex rather than the neat imidacloprid was utilized for PP filament yarn production.

In order to verify the presence of IMI within the PP filament yarn, filaments were subjected to dichloromethane extraction. HPLC analysis showed that 80 % of the IMI could be recovered. Afterwards, IMI release profile of PP/IMI-β-CD (97/3 w/w) filament yarns was studied. *Figure 7* presents the HPLC chromatograms at different time intervals. The peak areas obtained at a retention time of 7.1 min were used to calculate the amount of IMI release based on the IMI loading and dilution factor. IMI release amounts from PP/IMI-β-CD filament yarns at different time intervals are given in *Table II*. According to *Table II*, a small amount of IMI (3.56 mg) was released on the 0^{th} day. This could be explained by the presence of residual IMI on the PP filament surface. IMI release percentages were calculated from release amounts and are plotted over time in *Figure 8*. This graph shows that imidacloprid release reached a plateau on the 17th day of the experiment. Thus, the IMI-β-CD inclusion complex incorporation into polypropylene extended the imidacloprid release time substantially when compared to that of the IMI-β-CD inclusion complex alone.

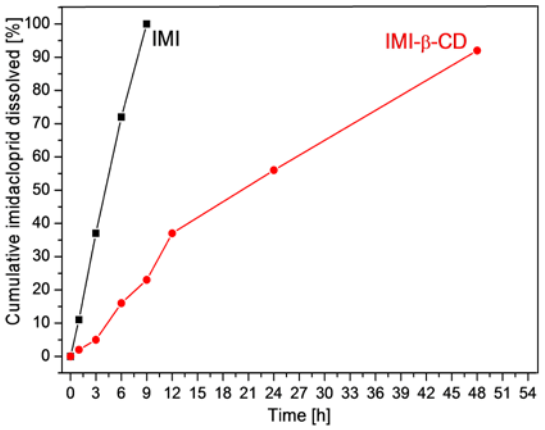

FIGURE 6. Cumulative imidacloprid dissolution profile of IMI and IMI-β-CD inclusion complex in distiled water.

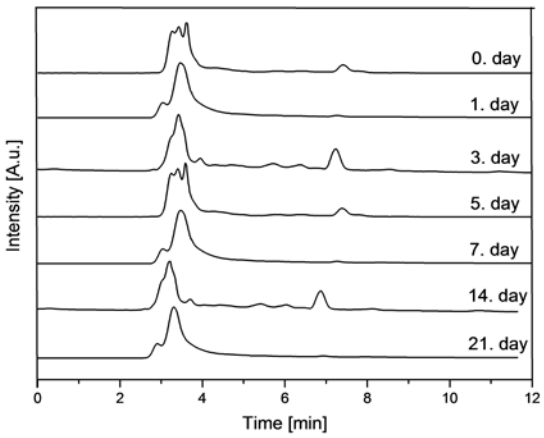

FIGURE 7. HPLC chromatograms PP/IMI-β-CD (97/3 w/w) filament yarns at different time intervals.

TABLE II. Imidacloprid release amount (mg) from PP/IMI-β-CD (97/3 w/w) filament yarns.

Time interval (day)	Release amount (mg)
0	3.56
1	12.97
3	7.56
5	8.25
7	15.44
14	21.40
21	3.35

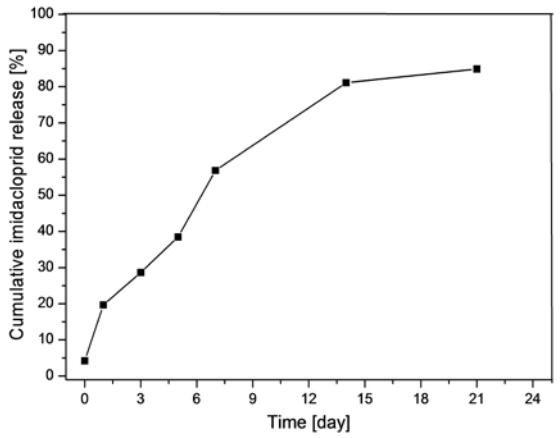

FIGURE 8. Cumulative imidacloprid release of PP/IMI-β-CD (97/3 w/w) filament yarns.

CONCLUSION

An inclusion complex of imidacloprid with β-cyclodextrin was successfully synthesized. The inclusion complex demonstrates improved thermal stability and controlled release properties. The imidacloprid-β-cyclodextrin inclusion complex was incorporated into polypropylene and filament yarns were produced. The filaments showed a prolonged release profile of imidacloprid (84 wt.% within 21 days), indicating promise for these materials in agrotextile applications.

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